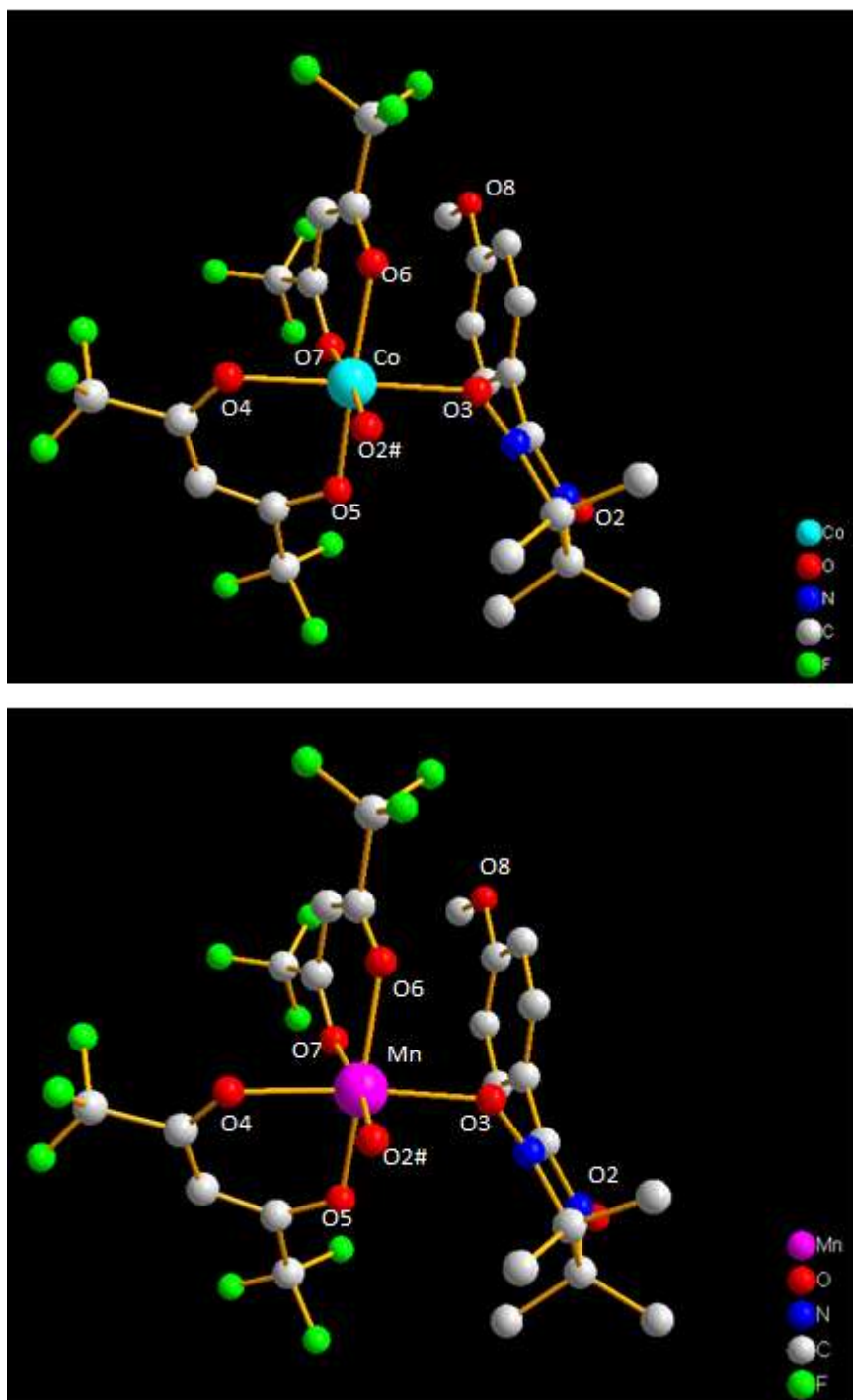


## **Supplementary Information**

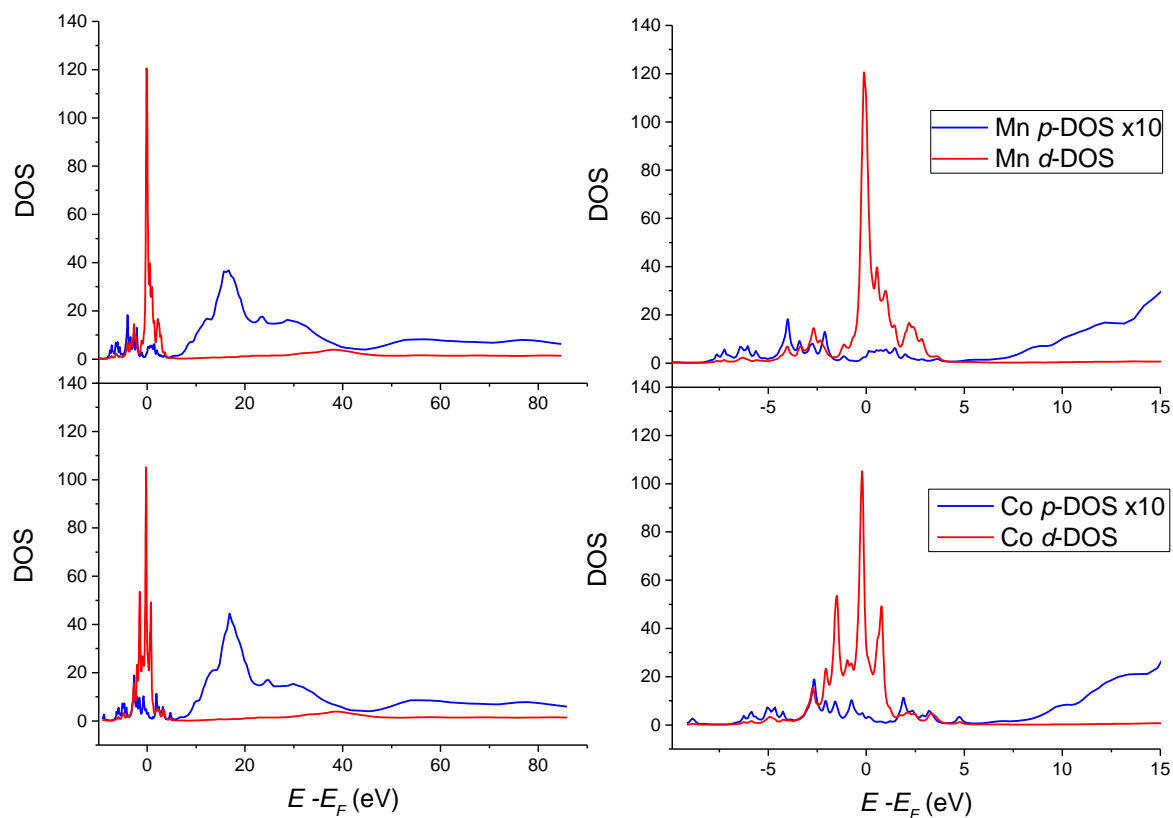
# **Strong magneto-chiral dichroism in a paramagnetic molecular helix observed by hard X-ray**

by

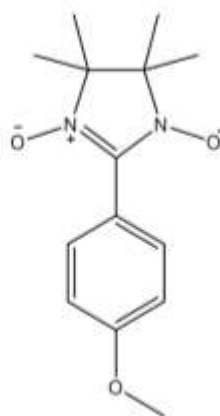
Roberta Sessoli, Marie-Emmanuelle Boulon, Andrea Caneschi, Matteo Mannini, Lorenzo Poggini,  
Fabrice Wilhelm, and Andrei Rogalev



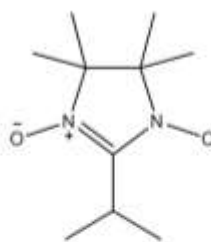
**Supplementary Figure 1.** View of the asymmetric unit of the Cobalt(II) (top) and Manganese(II) (bottom) helices of formula  $[M(\text{hfac})_2\text{NITPhOMe}]_\infty$ . The hydrogen atoms have been omitted for the sake of clarity. Colour code in the legend. The octahedron around the metal ions is completed by the O2 atom of a neighbour radical labeled as O2#.



**Supplementary Figure 2.** Projected Density of States on  $p$ -type orbitals (blue, intensity multiplied by 10) and  $d$ -type orbitals (red) calculated for the  $[\text{Mn}(\text{hfac})_2\text{NITPhOMe}]_\infty$  (top) and  $[\text{Co}(\text{hfac})_2\text{NITPhOMe}]_\infty$  (bottom) as described in the main text. On the right the region around the Fermi energy is enlarged. The contribution of  $s$ -type orbitals has been omitted for the sake of clarity as these orbitals do not contribute to the observed signals.

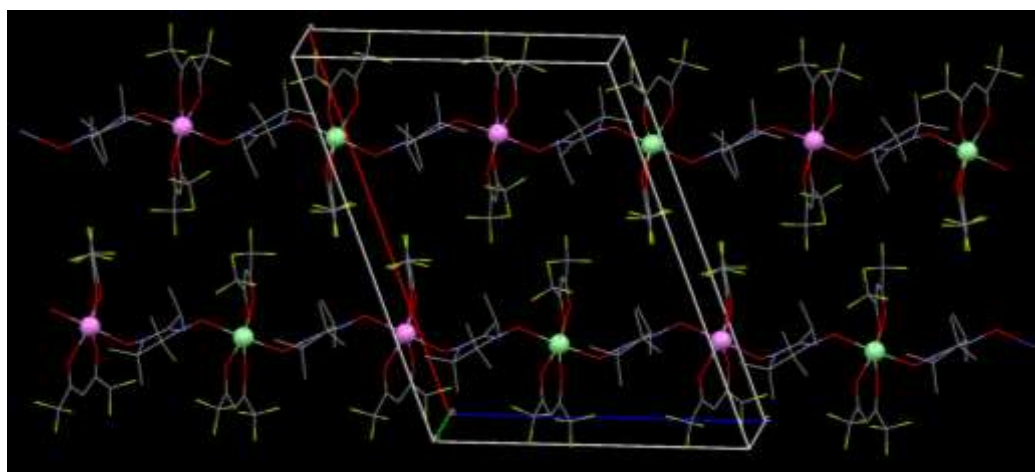


**NITPhOMe**

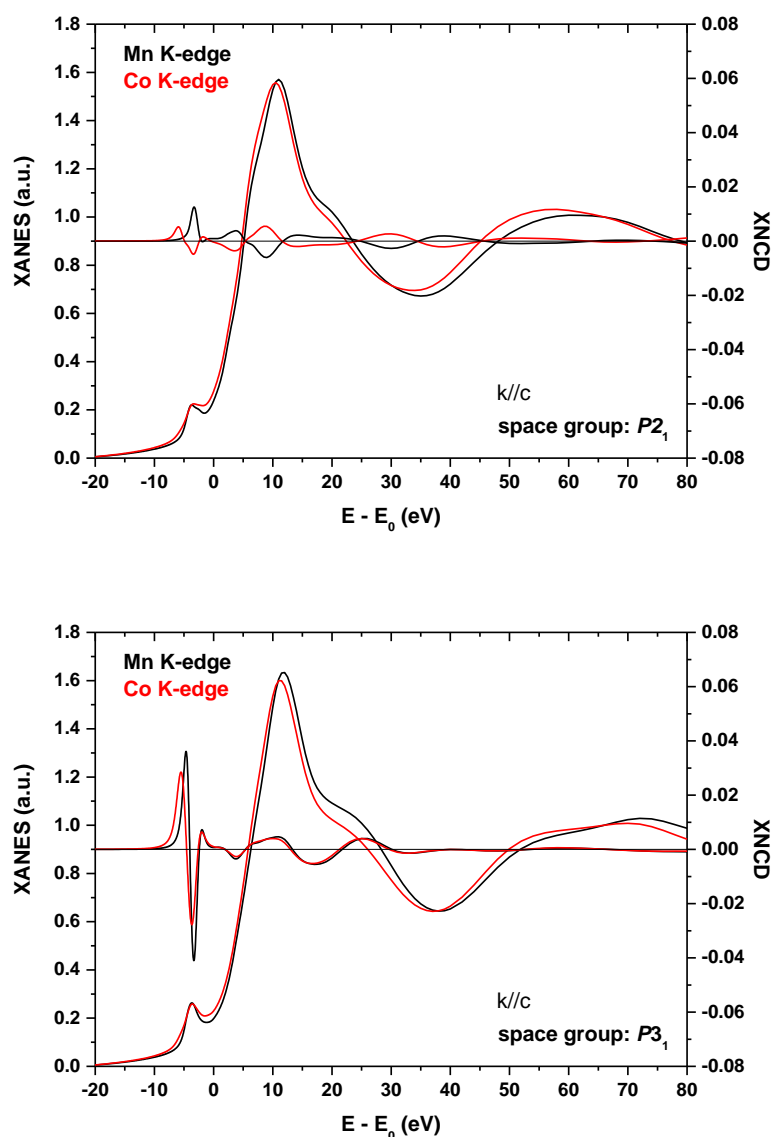


**NITiPr**

**Supplementary Figure 3.** Schematic structure of the nitronyl-nitroxide radicals present in the  $P3_1$  structure  $[M(hfac)_2NITPhOMe]_\infty$  (left) and in the  $P2_1/c$  structure  $[Mn(hfac)_2NITiPr]_\infty$  (right).



**Supplementary Figure 4.** View of the structure of the  $[Mn(hfac)_2NITiPr]_\infty$  chain compound. Large green and pink spheres represent Co and Mn atoms artificially segregated in the two acentric sublattices employed in the additional calculations. Colour code for other atoms: carbon atoms, grey; fluorine, yellow; oxygen, red; nitrogen, blue. Hydrogen atoms have been omitted for the sake of clarity, red, green and blue axis represent  $a$ ,  $b$  and  $c$  crystallographic axis, respectively.



**Supplementary Figure 5.** Top) Calculated XANES and XNCD spectra at the Mn and Co K-edge using the method described in the main text and assuming the artificially segregated structure of  $[M(\text{hfac})_2\text{NITiPr}]_\infty$ ,  $M=\text{Mn, Co}$ , depicted in Supplementary Figure 4, corresponding to the  $P2_1$  space group for each metallic atomic species. Bottom) Same calculations performed with the structures of the investigated  $[M(\text{hfac})_2\text{NITPhOMe}]_\infty$  samples, corresponding to the  $P3_1$  space group. Energies are reported as the difference from the corresponding edge values ( $E_0$ ). The XNCD spectra at Mn and Co edge have opposite sign, being the two artificial sub-lattices related by the inversion centre. The comparison with the calculated XNCD for the crystallographic structures of  $[M(\text{hfac})_2\text{NITPhOMe}]_\infty$  in the  $P3_1$  space group evidences for the latter a significantly larger dichroic signal at the pre-edge (slightly negative energy values) corresponding to transitions to partially occupied  $3d$  orbitals.

**Supplementary Table 1.** Bond distances in (Å) and bond-angles (°) around the metal centre of the [M(hfac)<sub>2</sub>NITPhOMe]<sub>∞</sub> helices, for M=Co and Mn. Atom labelling is described in Supplementary Figure 1.

Bond distances		
	<b>M=Co</b>	<b>M=Mn</b>
M-O2#	2.111	2.143
M-O3	2.097	2.121
M-O4	2.058	2.141
M-O5	2.040	2.125
M-O6	2.029	2.090
M-O7	2.085	2.194

Bond angles		
O2#-M-O3	85.24	86.92
O2#-M-O4	87.62	85.40
O2#-M-O5	97.15	99.67
O2#-M-O6	95.51	100.09
O3-M-O4	172.70	171.90
O3-M-O5	92.34	93.81
O3-M-O6	84.31	85.76
O3-M-O7	99.11	100.93
O4-M-O5	90.00	84.96
O4-M-O6	94.93	98.10
O4-M-O7	88.05	86.86
O5-M-O6	166.59	160.18
O5-M-O7	81.90	82.27
O6-M-O7	85.81	78.34

### Supplementary Note 1

The XANES and XNCD spectra were also calculated for a virtual acentric structure not comprising the three-fold screw axis. The atomic coordinates of the compound [Mn(hfac)<sub>2</sub>NITiPr]<sub>∞</sub> differing from the investigated one only for the organic residue on the radical as shown in Supplementary Figure 3.

As the [Mn(hfac)<sub>2</sub>NITiPr]<sub>∞</sub> chain compound crystallizes in the centric P2<sub>1</sub>/c monoclinic space group no optical activity is expected. However, the crystallographic coordinates have been modified by assuming P2<sub>1</sub> symmetry and substituting Mn atoms with Co atoms on the sites related by the inversion centre, as shown in Supplementary Figure 4. Given the atomic character of the employed X-ray spectroscopy the XANES and XNCD spectra can be calculated at the Mn and Co K-edge through the FDMNES code (see main text).